The Reduction of Metallic Oxides with Hydrogen at High Pressures.

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[PLATE 1.]

INTRODUCTION.

The equilibrium relation in the reaction between a metallic oxide and hydrogen is determined at any given temperature by the concentration of the hydrogen and that of the water vapour produced by the reduction. Thus, if in the equation:—

$$MeO + H_2 \leftrightarrows Me + H_2O,$$

C denotes the concentration of the hydrogen and C′ that of the water vapour, we have the relation:—

$$C/C' = K,$$

where K is a constant at any given temperature. If C/C' can be arranged to be greater than K, the reaction expressed in the above equation proceeds from left to right.

This state of affairs may be realised:—

(*a*) By increasing the pressure of the hydrogen present.

(*b*) By diminishing the pressure of the water vapour formed during the reaction.

(*c*) If the reaction is endothermic, by raising the temperature, when the value of K is diminished according to van't Hoff's equation,

$$\frac{d\,ln\,K}{dT} = \frac{-Q_{(T)}}{RT^2},$$

whence $ln\,K = Q_{(T)}/RT + \text{const.}$

Here $Q_{(T)}$ represents the heat absorbed by the progress of the reaction at the temperature in question. If therefore $Q_{(T)}$ is positive, or the reaction is endothermic, K is diminished with the rise in temperature and the change shown in the above equation proceeds from left to right.

The work described in the present paper was undertaken with the object of seeing how far these theoretical considerations can be applied practically, and also of preparing pure metals or lower oxides of metals free from many impurities which are unavoidably present in such substances when prepared by other means.

EXPERIMENTAL.

Part 1.—*Description of Apparatus.*

One of the high-pressure electric furnaces used was similar in design to that used by Pring and Fairlie* in the experiments on the synthesis of hydrocarbons.

A photograph of the furnace in use is shown in Plate 1, fig. 1. This furnace enabled the use of pressures up to 200 atmospheres.

Hydrogen for these experiments was obtained commercially in cylinders at a pressure of 150 atmospheres. The gas, of about 99·8 per cent. purity, was prepared by electrolysis, the residual gas consisting of nitrogen.

For higher pressures, a furnace was used which was designed by Prof. E. Petavel and kindly placed by him at our disposal for this work. A photograph of this furnace is shown in fig. 2. It has a much smaller capacity than that first described, but has been tested to a pressure of 1500 atmospheres.

For the present experiments, hydrogen at about 100 atmospheres pressure was admitted to a subsidiary cylinder and from here was compressed into the furnace by forcing glycerine in at the base of the cylinder with a hydraulic pump. By repeatedly filling this cylinder and then compressing into the furnace, pressures up to 900 atmospheres were obtained. In both types of furnace, the initial pressure applied was always increased considerably on heating.

The production of the necessary high temperature was the chief experimental difficulty to be overcome. At the first attempt, "nichrome" wire, M.P. about 1400°, was wound round a small fireclay crucible containing the metallic oxide and the whole packed round with dry magnesia. On sending a current through the wire, it fused long before the required temperature could be attained in the crucible for the reduction of any refractory oxide. The next attempt was made with a platinum tube 6 inches long and 1 inch diameter, which was clamped by one end vertically in the nickel cup at the bottom of the pressure furnace. The upper end of the platinum tube was packed into a massive brass ring by strips of nichrome foil, the brass ring itself being surrounded by strips of copper foil making good electrical connection with the sides of the furnace. The space between the platinum tube and the walls of the furnace was packed with dry magnesia, and a current of 300 ampères passed through the tube.

It was then found that the tube could not be heated uniformly, as the smallest irregularity of thickness produced local superheating and melting of the platinum tube in patches before the required temperature could be attained in a small crucible placed inside the tube.

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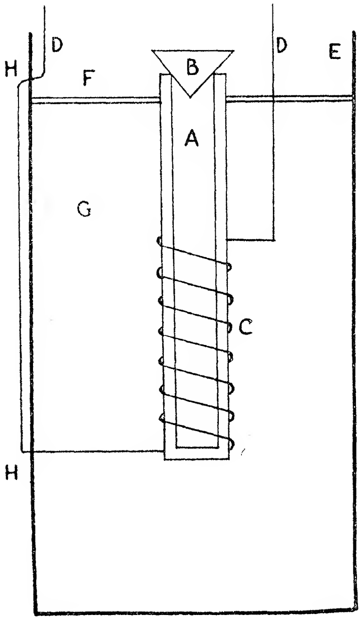
* 'Trans. Chem. Soc.,' vol. 101, p. 95 (1912).

The next attempt was made with tungsten wire 0·2 mm. diameter, as the heating body, this being wound round a small fireclay crucible, 2½ inches long and ½ inch diameter. The small crucible was placed in a larger crucible, 1 inch diameter, and the space between packed with magnesia. The whole was now placed in the pressure furnace, a rhodium-platinum thermo-couple introduced, the air displaced by hydrogen, and a current of 8 ampères, at 60 volts, passed through the wire. A temperature of 1200° C. was obtained but the crucible was cracked and partly melted.

A thicker wire, 0·25 mm., wound round a crucible of fused magnesia and placed in a larger outer vessel packed with dry magnesia enabled a temperature of over 1500° to be obtained, but after once heating the tungsten wire became so brittle that it was impossible to remove the crucible from the furnace without breaking the wire.

Fig. 3



After several further trials the apparatus shown in fig. 3 enabled a temperature of over 2000° C.[*] to be obtained inside the crucible, while with reasonable care the whole could be removed from the furnace and the contents of the crucible examined without breaking the tungsten wire. A is the magnesia or alumina crucible containing the metallic oxide; B a small cone made of fused magnesia, serving as a crucible cover, but having small V slots filed in it to allow more free diffusion of gas; C the tungsten wire, 0·5 mm. thick, and 50 cm. in length, which was first wound round a glass tube of slightly smaller diameter than the crucible, and then "sprung" on to the crucible, fitting into a spiral groove which had previously been filed into the walls of the crucible. The nickel wire leads D, D, were twisted round the ends of the tungsten wire and a small extra piece of tungsten wire twisted round the junction and continued for about 1 inch along the main wire, as it was found that fusion of the tungsten was specially liable to take place near the junction with the nickel. The outer vessel E was a porous earthenware battery pot, through the sides of which small holes H, H, were drilled. This was heated to redness, cooled, filled with freshly ignited magnesia powder, and covered with an asbestos disc F.

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[*] Temperatures up to 1600° C. were measured by means of the platinum : platinum-rhodium thermo-couple already referred to. Temperatures above this were estimated partly by observation of the strength of current passing through the tungsten wire and comparison with that used for producing the lower measured temperatures, and partly by examination of the crucible after cooling. In all the successful experiments the magnesia or alumina crucibles were partially melted and rendered semi-transparent, and

With this apparatus, all the successful experiments described in this paper were carried out, using hydrogen pressures up to 150 atmospheres.

Two other forms of apparatus were tried which it is perhaps worth while describing here, though the results obtained were not satisfactory.

In the one form, the second type of furnace, constructed to stand pressures up to 1500 atmospheres was used, the arrangement of tungsten and crucible being much the same as before, but owing to the smaller capacity of the furnace, the outer vessel E could not be used. To keep the heat in round the crucible, the whole available space in the furnace was packed with magnesia. Green chromium oxide was placed in the crucible and hydrogen forced in by means of the glycerine force pump and compression chamber until the pressure was 500 atmospheres. On heating the tungsten wire, this pressure rose to 880 atmospheres. Under these conditions a small quantity of the Cr_2O_3 was changed to the black CrO, and in a further experiment, MnO_2 was partly changed to black crystalline MnO after four hours' heating. The weak reduction here was evidently due to insufficient condensation of water. The sides of the furnace were kept cold by a system of tubes with water flowing through them, but the slow diffusion of the water vapour from the crucible through the magnesia prevented its pressure being reduced sufficiently by condensation on the furnace walls.

In the other form of apparatus an attempt was made to reduce the oxides by heating at very low pressures.

A small pressure furnace was connected to a Gaede pump with a McLeod gauge attached, and the Gaede pump to a Fleuss pump worked by a $\frac{1}{8}$-H.P. electromotor. The Gaede pump was also worked by a small electromotor.

The difficulties in the way of obtaining a high temperature in this case were very great. If magnesia was used to insulate the crucible, the absorbed

it was evident that a temperature very close to the melting point of magnesia or alumina was attained in the interior of the crucible. There is still some uncertainty as to the melting point of magnesia. The measurement is made difficult by the marked volatilisation which occurs below the melting point when at atmospheric pressure. It was shown by Greenwood ('Proc. Roy. Soc.,' A, vol. 82, p. 406 (1909)) that this melting point is higher than 2500°. Recent work by Kanolt ('Bull. Bur. Standards,' vol. 10, p. 295 (1914)) estimates the value to be 2800° for magnesia and 2050° for alumina.

oxygen attacked the tungsten wire and also prevented the pressure from being reduced by coming off very slowly as the magnesia was heated.

An attempt was made to avoid the use of magnesia by surrounding the crucible with a quartz tube, and a hard glass tube outside that, the whole being placed in a porous pot and this in the furnace. A pressure of 0·001 mm. could be obtained while cold but not while heating was proceeding. The temperature could not be raised above 1000° C. under these conditions. In spite of these difficulties, a small quantity of Cr_2O_3 was reduced to CrO, and MnO_2 to MnO, but since at the above pressure it would be necessary to remove 150,000 litres of gas from 1 grm. of Cr_2O_3, a process requiring at least four months' continuous working, further experiment on these lines was abandoned.

Part 2.—*Reaction between Refractory Oxides and Hydrogen at High Temperatures and Pressures.*

Experiments on the following oxides were carried out with the apparatus shown in fig. 1:—

Cr_2O_3, MnO_2, V_2O_5, Nb_2O_5, CeO_2, U_3O_8, TiO_2, ZrO_2, Y_2O_3, ThO_2.

Chromium Oxide.—A sample of Merck's specially pure chromium oxide was heated to redness in a quartz crucible, cooled in a desiccator, and about 2 grm. placed in the experimental crucible of magnesia or alumina. The air was displaced from the furnace by passing in hydrogen to about 30 atmospheres pressure and after a time allowing it to escape. The hydrogen pressure was then raised to 100 atmospheres and a current of 17 amperes, at 40 volts, passed through the tungsten wire, which in all cases was about 50 cm. in length. The walls of the furnace were cooled by a current of cold water passing round them.

After five hours' heating, it was allowed to cool and the furnace opened. The greater part of the Cr_2O_3 had been reduced to the monoxide, which was well crystallised in needle-shaped crystals. At the bottom of the crucible, a small quantity of metallic chromium was found mixed with the monoxide.

The temperature attained was very high, over 2000° C. near the bottom of the crucible. The crucible itself was partially fused and shrunk considerably where the temperature had been greatest, while the magnesia packing was volatilised near the tungsten wire and condensed again in small transparent crystals forming a hollow crust round the lower part of the crucible.

A photograph of a crucible after use in this way, with part of the hollow crust broken off, is shown in fig. 4, Plate 1.

Though small fragments of pure chromium could be picked out from the broken mass, it was considered advisable to further improve the conditions in order that a pure sample of metallic chromium free from oxide could be obtained. After many trials, the following conditions were found essential to render the reduction complete. The crucible used must not be too narrow in proportion to its depth, otherwise the diffusion necessary takes place too slowly. A crucible ½ inch diameter and 3 inches long was found to be most suitable.

To reduce the pressure of the water vapour a small iron vessel containing crumpled sodium wire was placed at the bottom of the furnace, where the temperature did not exceed 40°.

Much longer time is needed to get rid of the last traces of oxide. Generally, in the most successful experiments, 24 to 27 hours was allowed for heating alone, with 130 atmospheres hydrogen pressure. Under these circumstances a good clean button of metallic chromium was obtained, the upper part being composed of small globules of metal matted together. No surface impurity was visible when this was examined under the microscope. Further experiments with this metal are described later.

Manganese Dioxide.—A sample of Merck's "Pure for Analysis" manganese dioxide was heated to redness in air before putting it into the pressure furnace.

The first experiments with this yielded a black, well crystallised mass of pure manganese monoxide, and if sodium is not used to reduce the pressure of aqueous vapour the reduction stops at this stage.

With the improved apparatus described above a small button of quite clean metallic manganese was obtained. This button had been completely fused, but was much smaller in size than had been expected. On examining the crucibles it was found that the fused oxides of manganese attack magnesia crucibles with the formation of green magnesium manganate, and alumina crucibles with formation of white transparent crystals of manganese aluminate. The metal itself is without action on either magnesia or alumina. Further experiments on the metallic manganese obtained are described later.

Vanadium Pentoxide.—The pentoxide was fused in a quartz crucible and the cooled mass broken up and placed in small lumps in a magnesia crucible. The preliminary heating was conducted very slowly to avoid, if possible, fusion taking place before reduction.

The first experiments yielded a mixture of a black iridescent body near the top of the crucible with a crystalline metallic substance near the bottom. The lumps of pentoxide had shrunk in size, but had not lost their original shape. Hence the preliminary reduction of the pentoxide takes place at a temperature below the melting point. The hydrogen pressure used in this case was 75 atmospheres, and the heating was continued for five hours. The black substance, which had a beautiful steel-blue iridescence, conducted electricity freely, and was probably the trioxide V_2O_3.

The silver-white metallic looking substance was evidently a crystalline form of the monoxide VO. This conducts electricity like a metal, is very hard though brittle, is readily soluble in nitric acid, dilute or strong, and, unlike the monoxide prepared in other ways, is insoluble in dilute or strong hydrochloric or sulphuric acid. Its chemical and physical properties seem to be identical with those of metallic vanadium, and only a quantitative estimation of the vanadium present was capable of proving that the substance really was the monoxide. This crystalline form of the monoxide does not appear to have been prepared before. A further experiment with improved conditions gave a mass of monoxide with clean well-formed crystals in the hottest part of the crucible, but further reduction could not be produced.

Uranium Oxide.—A sample of pure U_3O_8 was heated to redness, cooled, and placed in a magnesia crucible as before. Several attempts were made to reduce this, but even with long continued heating to a temperature of over 2500° C. with 150 atmospheres hydrogen pressure, the reduction could not be carried further than the dioxide UO_2. This was in the form of a black semi-crystalline substance, insoluble in acids, with the exception of strong nitric acid, in which it dissolved with evolution of brown fumes. When heated in the air on platinum foil, it glowed, swelled up, and fell to a black powder. No evidence of the presence of metal could be obtained. Some magnesium uranate appears to be formed at the same time.

Thoria, Zirconia, and Yttria.—Samples of each of these were treated in the same way as the uranium oxide, but no evidence of reduction could be obtained.

Titanic Acid.—Pure titanic acid was heated in a magnesia crucible with a pressure of 130 atmospheres of hydrogen. Some of the substance was absorbed by the magnesia of the crucible, yielding a bluish-white magnesium titanate round the upper part of the crucible. The remainder was converted into a rod of well crystallised black monoxide, TiO, which was completely coated with the gold-coloured mono-nitride, evidently formed from the small quantity of nitrogen which is always present in commercial "pure" hydrogen.

Cerium Oxide.—This oxide, CeO_2, was obtained by igniting the pure nitrate. When treated as before, with 130 atmospheres hydrogen pressure, it was completely converted into the pale yellow-green sesquioxide Ce_2O_3, a body which is difficult to prepare by other methods. No further reduction could be induced by this method.

Niobium Pentoxide.—This was readily reduced to the tetroxide, but further reduction takes place very slowly. After long continued heating at 120 atmospheres hydrogen pressure a black amorphous substance was obtained which became incandescent on heating in the air, and probably consists of a mixture of the dioxide and tetroxide.

Part 3.—*Nature of Products.*

Only chromium and manganese were obtained in the metallic states. The hydrides of manganese and chromium, if they exist at all, must be very unstable substances, and cannot be formed at the high temperatures used in the furnace.

The nitrides of both metals are almost black powders when prepared by passing nitrogen over the metals at a red heat, but manganese nitride is readily decomposed by hydrogen with the formation of ammonia. It is practically certain that, with the high pressures of hydrogen used, chromium nitride is decomposed in the same way, for examination of these metals under the microscope revealed no trace of any dark coloured compound.

Any traces of combined or occluded gas would also be removed by the subsequent heating in high vacua, to which these metals were subjected.

Since the purest oxides obtainable were used for the production of these metals, and no impurity other than hydrogen and nitrogen introduced, it seems probable that the metals obtained were in a high degree of purity.

Part 4.—*Melting-point Measurements.*

Burgess and Waltenberg* were unable to procure pure manganese or chromium. They showed that observation of the melting of very small pieces of metal on electrically heated metallic strips furnished a very delicate test as to the purity of the metal, mere traces of impurity rendering the melting point indefinite, and making the flowing of the liquid metal sluggish. In order to make use of this as a test for the purity of the samples obtained in the previous work, a platinum strip, 3 inches by ½ inch, was held by two water-cooled copper tubes in the centre of a round flask with three necks, two of which supported the copper tubes, while the third served for the introduction of the crushed metal on a glass spoon, and also carried a side tube, which could be connected either to a Gaede pump or to a hydrogen generator. A microscope magnifying 25 diameters was mounted above the flask, and a Wanner optical pyrometer by the side of the microscope, looking vertically down on the horizontal strip of platinum. Measurements of the melting points of chromium and manganese were made by means of this apparatus both in a good vacuum (0·0003 mm.) and in an atmosphere of pure dry hydrogen obtained by the electrolysis of sodium hydroxide solution. The temperature of the platinum could be accurately regulated by means of two carbon rheostats, arranged in series with each other, and in parallel with a wire resistance frame. The melting points observed were identical *in vacuo* and in hydrogen.

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* 'Bull. Bur. Standards,' vol. 10 (1913).

In the case of manganese the melting point was extremely sharp, small fragments melting so suddenly as to give the impression of a drop of liquid falling from a small height and splashing out over the surface of the platinum, while at the same time slightly larger fragments were unmelted. The larger fragments, however, melted in the same way when the temperature was raised not more than 5° C. further.

The mean of 10 determinations, corrected to "black body" temperature, gave: melting point of pure manganese, $1230° \pm 5°$ C.

The melting point of chromium was found to be equally sharp, but more difficult to observe, partly on account of the higher temperature, and partly on account of the curious fact that the chromium at first does not splash out over the surface of the platinum, but forms a little globule on the platinum without "wetting" it. On looking through the microscope, therefore, the small irregular fragments of chromium are seen to suddenly "jump" to the globular state. As might be expected in this case, the larger fragments required a greater elevation of the temperature above the true melting point than corresponding fragments of manganese, but, if the fragments were below a certain size, they all appeared to melt at the same temperature. After the fragments had melted they slowly alloyed with the platinum, more quickly if the temperature was raised.

The mean of 10 determinations, corrected to "black body" temperature, gave: melting point of pure chromium, $1615° \pm 15°$ C.

Part 5.—*Summary and Conclusions.*

Metallic oxides have been heated to temperatures of 2500° C. in dry hydrogen at pressures up to 150 atmospheres, water vapour being partly removed by metallic sodium.

The following oxides were reduced to metals:—

Cr_2O_3 to Cr. MnO_2 to Mn.

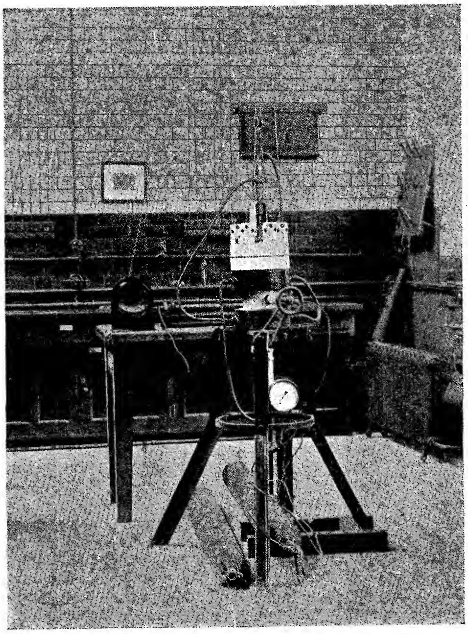

Fig. 1.

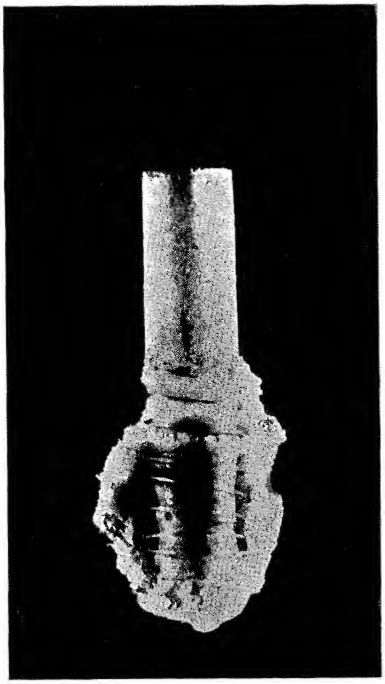

Fig. 4.

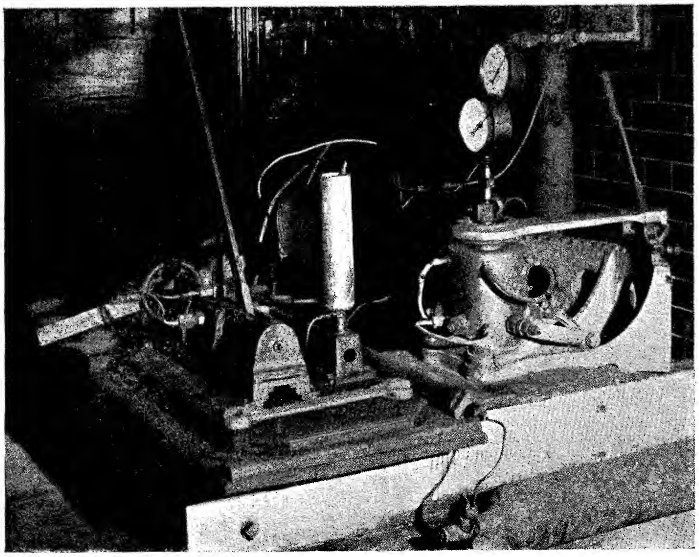

Fig. 2.

The following oxides were reduced to lower oxides:—

V_2O_5 to VO. TiO_2 to TiO.
Nb_2O_5 to NbO. CeO_2 to Ce_2O_3.
U_3O_8 to UO_2.

The following oxides were unchanged:—

Al_2O_3, MgO, ZrO_2, Y_2O_3, ThO_2.

The metals obtained, chromium and manganese, are probably purer than those prepared by any of the methods used hitherto.* This supposition is supported by the sharp nature of their melting points, a feature which has not been observed with samples prepared by other methods.

Part of the incidental expenses of this investigation has been met by a grant kindly made by the Chemical Society.

Discontinuous Fluid Motion Past a Curved Boundary.

By H. Levy, M.A., B.Sc., Carnegie Research Fellow, late 1851 Exhibitioner of University of Edinburgh.

(Communicated by Prof. A. E. H. Love, F.R.S. Received November 2, 1915.)

Although many writers have devoted their attention to the problem of the motion of a fluid past a curved boundary, no method so simple, yet so effective, as that developed for the case of a plane barrier by Kirchhoff† and others, and since elaborated by Mitchell,† Love,† Bryan and Jones,† etc., has been discovered for the more general case. Within the past few years a group of mathematicians in Italy and in France, in particular Levi-Civita, Cisotti, and Villat, and J. G. Leathem in this country, have published notable advances on this subject. In aeronautics alone recent developments have shown the practical necessity for an effective discussion of the case where the plane is cambered.

In this paper I propose to show how two-dimensional problems of the motion of a curved surface through a fluid, or the efflux of fluid through an orifice in a vessel of any shape, may be solved, how to find the form of the free stream-line, and how the components of resistance may be calculated

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* The purest samples examined by Burgess and Waltenberg contained 97–98 per cent. manganese and 98–99 per cent. chromium, and melted at 1255° and 1520° respectively.

† See Bibliography.

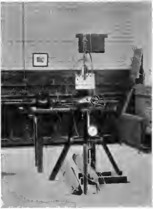

Fig. 1.

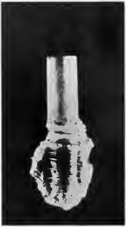

Fig. 4.

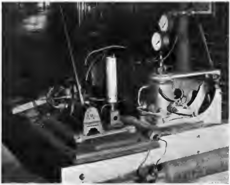

Fig. 2.